Growth of In-rich InGaN Quantum Dots (QDs) by Metalorganic Chemical Vapor Deposition (MOCVD)

Euijoon Yoon

School of Materials Science and Engineering, Seoul National University, Sillim-dong, Gwanak-gu, Seoul 151-742, Korea

tel: +82-2-880-7169, fax: +82-2-875-0679, e-mail: eyoon@snu.ac.kr

ABSTRACT

We successfully grew In-rich InGaN/GaN quantum dots (QDs) by metal-organic chemical vapor deposition. Growth at low temperatures below 700 ^oC made it possible to obtain In-rich InGaN layer with In content over 70 % and we confirmed it by electron probe microanalysis (EPMA) and x-ray diffraction (XRD). We obtained uniform QDs with density of 1.3 x 10^{10} /cm^2 by optimizing growth conditions. The density of QDs was further increased to 3.0 x 10^{10} /cm^2 with AlGaN barrier layer. Strong photoluminescence (PL) emission from In-rich InGaN/GaN QDs was observed at room temperature and emission wavelength was varied from 404 nm to 454 nm depending on QD size. It is strongly suggested that QDs leads to higher radiative recombination efficiency from temperature dependent PL measurement.

Keywords: In-rich InGaN, quantum dots, MOCVD

1. INTRODUCTION

InGaN quantum dots (QDs) have attracted much attention for their potential application for the active layers of laser diodes (LDs) and laser emitting diodes (LEDs) [1-3]. QDs are expected to provide carrier localization centers with negligible compositional fluctuation. Although it has been reported that the strong emission of the InGaN quantum wells (QWs) was attributed to the dot-like localization states induced by the compositional fluctuations [4], fabrication of artificially formed QD structures in nitride semiconductors is required especially in materials systems without compositional fluctuation. Until now, several InGaN QD results have been reported [5-8]. However, most of them reported Ga-rich InGaN QDs with In content below 50 %. From the viewpoint of misfit strain, In-rich InGaN QDs with In content over 50 % is more favorable to form high density 3-dimensional structures than Ga-rich InGaN QDs due to the large lattice mismatch between InGaN and substrates such as GaN or AlGaN. In addition, according to the recent reports about the InN band gap as low as 0.7 eV [9-11], the small change in dot height or In composition would cause the large shift of emission wavelength. From our earlier studies on In-rich InGaN quantum structures such as QWs and QDs [12-13], even near ultraviolet (UV) emission was possible through the huge carrier confinement in such quantum structures with very small height. In this point of view, In-rich InGaN/AlGaN QD structures, with their larger band offset and stronger carrier confinement, are more favorable to induce large blue-shift in emission wavelength than In-rich InGaN/GaN QD structures. Therefore, In-rich InGaN QDs are expected to be one of candidate materials for future optoelectronic devices of which emission wavelength can cover from UV to visible region. In this report, we report the growth of In-rich InGaN QDs with In content about 80 % and the control of their structural and optical properties by changing growth conditions.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
28 JUL 2006	**Final Report (Technical)**	**15-11-2005 to 30-03-2006**

4. TITLE AND SUBTITLE
Growth of In-rich InGaN/GaN Quantum Dots (QDs) by Metalorganic Chemical Vapor Deposition (MOCVD)

5a. CONTRACT NUMBER
FA520905P0108

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Euijoon Yoon

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Seoul National University,San 56-1, Shilllim, Kwanak,Seoul 151-742,KOREA,KE,151-742

8. PERFORMING ORGANIZATION REPORT NUMBER
AOARD-054007

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
The US Resarch Labolatory, AOARD/AFOSR, Unit 45002, APO, AP, 96337-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AOARD/AFOSR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AOARD-054007

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
In-rich InGaN/GaN quantum dots (QDs) were successfully grown by metal-organic chemical vapor deposition. Growth at low temperatures below 700 C made it possible to obtain In-rich InGaN layer with In content over 70 % and was confirmed by electron probe microanalysis (EPMA) and x-ray diffraction (XRD). Uniform QDs were obtained with density of 1.3 x 1010 /cm2 with optimizing growth conditions. The density of QDs was further increased to 3.0 x 1010 /cm2 with AlGaN barrier layer. Strong photoluminescence (PL) emission from In-rich InGaN/GaN QDs was observed at room temperature and emission wavelength was varied from 404 nm to 454 nm depending on QD size. It was concluded that QDs showed higher radiative recombination efficiency from temperature dependent PL measurement.

15. SUBJECT TERMS
III-N Compounds, Metalorganic Chemical Vapor Deposition (MOCVD)

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**		**8**	

2. EXPERIMENTAL

InGaN QD structures were grown by low pressure metalorganic chemical vapor deposition (LP-MOCVD). Trimethylaluminum (TMAl), trimethylgallium (TMGa), trimethylindium (TMIn), and ammonia were used as Al, Ga, In and N sources, respectively. The growth procedure and the characteristics of the GaN buffer layer can be found in Ref. 14. 2-μm-thick GaN buffer layers were grown on (0001) sapphire substrates at 1080 ^{o}C before the growth of In-rich InGaN QD structures. During the InGaN QD growth, the growth temperature of InGaN QD layers were varied in the range of 640 ~ 730 ^{o}C. TMGa, TMIn and ammonia flow rates were kept at 3 μmol/min, 10 μmol/min and 4 slm, respectively. QD growth time was varied from 2 s to 8 s. During the growth of InGaN, N_2 was used as a carrier gas instead of H_2. Then, 20-nm-thick GaN capping layer was grown at the same growth temperature as that of InGaN QD growth. Other growth conditions for the thick GaN buffer layers and the GaN capping layers were also fixed for all samples. After all the growth sequences were over, the sample was cooled down to room temperature under N_2 and ammonia atmosphere with the same flow rates as that of preceding growth step. In-rich InGaN QDs were also grown on crack-free AlGaN barrier layers. The thickness of the AlGaN barrier layer was 100 nm and the Al content in AlGaN barrier layer was 30 %. The growth pressure was maintained at 300 Torr throughout the whole process except for AlGaN barrier layer growth, which was performed at 50 Torr.

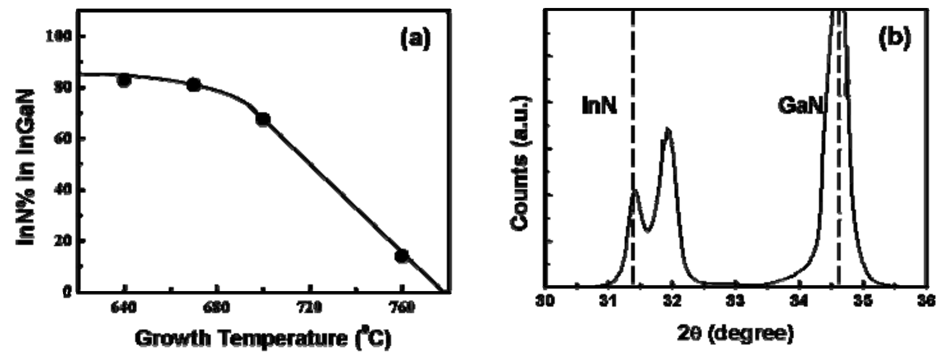
Thick InGaN layers were grown directly on sapphire substrates for precise determination of In content by electron probe microanalysis (EPMA). We also estimated the In content by x-ray diffraction (XRD) and reciprocal space mapping (RSM). Al content in AlGaN barrier was measured by Rutherford backscattering spectrometry (RBS). Structural properties of In-rich InGaN QD structures were characterized by atomic force microscopy (AFM), and transmission electron microscopy (TEM). Optical properties of In-rich InGaN QDs on GaN and In-rich InGaN QDs on AlGaN were examined by photoluminescence (PL) and temperature dependent PL using a He-Cd laser (325 nm) and a Nd:YAG laser (266 nm) as a pumping source, respectively.

3. RESULTS and DISCUSSION

3.1. Compositional analysis of InGaN layer

To determine the In incorporation ratio in InGaN, we grew thick InGaN layers at various growth temperatures and their In contents were determined by EPMA. It is generally accepted that In incorporation in InGaN layer is very sensitive to growth temperature due to the extremely high equilibrium vapor pressure of InN [15]. We varied the InGaN growth temperature from 640 ^{o}C to 760 ^{o}C. Indium contents in InGaN layers are shown in Fig. 1 (a). They were about 20 % when grown at 760 ^{o}C; however, they increased abruptly to about 80 % with lowering growth temperature to 640 ^{o}C. Especially below 700 ^{o}C, In incorporation ratio was similar to the input gas phase ratio of TMIn to TMGa (10:3) and we could obtain In-rich InGaN layers with In content over 70 %. We speculate that, in this work, In contents in InGaN layers were controlled by In desorption which is strongly dependent on growth temperature. Formation of In-rich InGaN layers was also confirmed by XRD. From the XRD measurement of $In_{0.8}Ga_{0.2}N$ layer that was grown at 640 ^{o}C, two major peaks at 31.4 ^{o} and 31.9 ^{o} appeared near the InN (0002) peak position (shown as a dotted line in Fig. 1 (b)). No indium metal droplet peaks were observed from all InGaN samples. The RSM shows two different InGaN peaks, InGaN(1) and InGaN(2). The vertical dashed line indicates the fully strained state and the sloped dashed line indicates the fully relaxed state. Figure 1(c) showed that the In-rich InGaN layer on GaN was found to be fully relaxed. Based on this RSM result, we calculated In contents for InGaN(1) and InGaN(2) using

Vegard's law, resulting in In contents of 82 % and 97 %, respectively. It is elucidated that these two RSM peaks originated not from non-uniform strain relaxation but from compositional fluctuation in In-rich InGaN layer. From the volume fraction of two peaks in XRD result as shown in Fig. 1(b), the average In content of InGaN was estimated to be about 87 %, which was close to the average In content of an InGaN on a sapphire substrate determined by EPMA. From XRD and RSM results, we confirmed the formation of In-rich InGaN layer and the compositional fluctuations in In-rich InGaN layers.



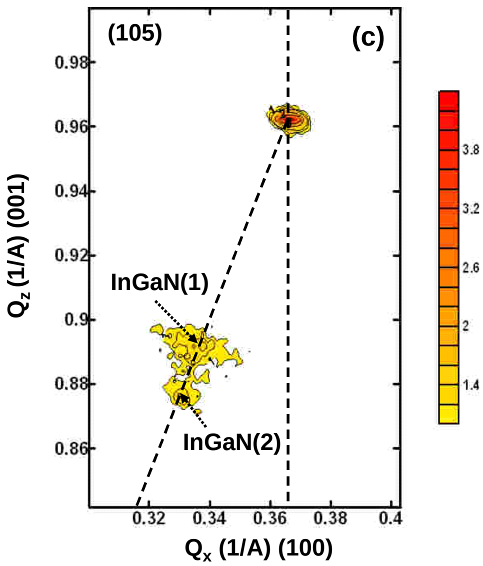


Fig. 1 (a) Changes in In content of InGaN layer with growth temperature estimated by EPMA, (b) XRD pattern and (c) RSM of InGaN grown at 640 ^{o}C, input gas phase ratio of TMIn to TMGa (10:3).

3.2. Growth of In-rich InGaN/GaN QD structure

InGaN layers were grown for 5 s without capping layers to study the surface morphology at various temperatures. AFM images of the grown InGaN layers are shown in Fig. 2. At 730 ^{o}C, InGaN surface showed 3-dimensional features, consisting of many islands with a density of 1.2 x 10^{8} /cm^{2}. The islands had average height of 0.63 nm and diameter of 150 nm, as shown in Fig. 2(a). However, as the growth temperature was lowered to the In-rich InGaN growth temperature of 650 ^{o}C, the average size of islands decreased enough to be considered as QDs. At the same time, the density of islands increased, as shown in Fig. 2(c). We believe that it would be due to the increased In composition and the reduced adatom diffusion length as growth temperature decreased. However, two types of QDs were observed at 650 ^{o}C. The sample consisted of large QDs with a density of 7.5 x 10^{8} /cm^{2} and small QDs with that of 5 x 10^{9} /cm^{2}. The average height and diameter of large QDs were 9.7 nm and 89 nm and those of small QDs were 1.16 nm and 78 nm. They arranged in rows along the terraces of an underlying GaN template.

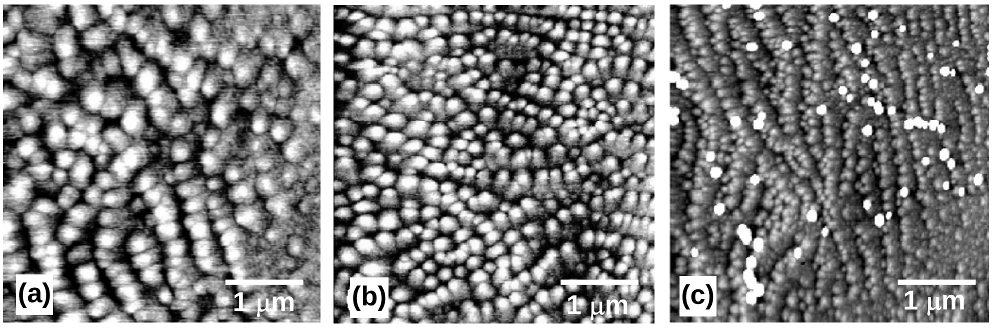


Fig. 2 4 μm x 4 μm AFM images of thin InGaN layers; grown for 5 s at (a) 730 °C, (b) 700 °C, and (c) 650 °C.

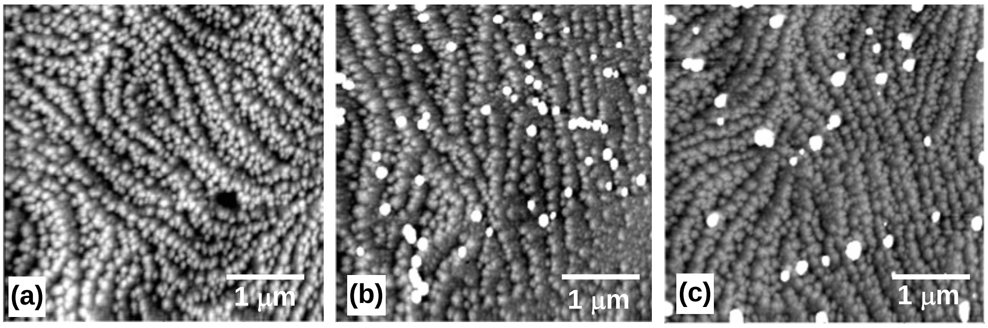


Fig. 3 4 μm x 4 μm AFM images of InGaN QDs grown on GaN at 650 °C for (a) 2 s, (b) 5 s, and (c) 8 s.

To get uniform In-rich InGaN QDs, we varied InGaN growth time from 2 s to 8 s at a fixed growth temperature at 650 °C. As the InGaN growth time increased to 8 s, the size of large QDs increased while maintaining that of small QDs as shown in Fig. 3(c). On the other hand, as the InGaN growth time decreased to 2 s, we could get uniform QDs without large QDs as shown in Fig. 3(a). The origin for the formation of large QDs is not certain at the moment; however, they might result from the coalescence process of small QDs. The small QDs may have slightly different In content due to the compositional fluctuation built in InGaN materials system. It is likely that QDs with higher In content would relax earlier. Once relaxed, they would absorb most of incoming In or Ga fluxes to grow abnormally. The formation of large QDs would be related with the presence of threading dislocations. Or, the presence of threading dislocations would induce the compositional fluctuation. To clarify the origin of large QDs, In-rich InGaN QD growth on high-quality GaN substrates (grown by hydride vapor phase epitaxy) is needed. In-rich InGaN QDs grown for 2 s had an average size of 1.2 nm in height and 65.7 nm in diameter. The aspect ratio (height/diameter) of the In-rich InGaN QDs was found to be below 0.1, which is similar to that of InN QDs [16], and very different from that of Ga-rich InGaN QDs [5-8]. The density of InGaN QDs could be further increased to 1.3 x 10^{10}/cm^2 by optimizing growth conditions, as shown in Fig. 3(a).

The formation of In-rich InGaN QDs on GaN was also confirmed by cross-sectional TEM analysis of the GaN-capped sample. The InGaN growth time and growth temperature of this sample were 2 s and 650 °C, respectively. To preserve the In-rich InGaN QDs, GaN capping

process was made without growth interruption at the same temperature with the QD growth. In Fig. 4, the dark contrast from In-rich InGaN QDs was observed between the GaN substrate and the low temperature (LT)-capped GaN layer. The height of QDs was estimated to be about 1~2 nm, which is consistent with the QD height deduced from AFM images. The cross-sectional TEM image also indicated that the crystalline quality of the GaN capping layer was relatively poor; the LT-GaN capping layer had the thickness fluctuations as well as high density defects. Process optimization to growth high quality LT-GaN capping layer is currently under way.

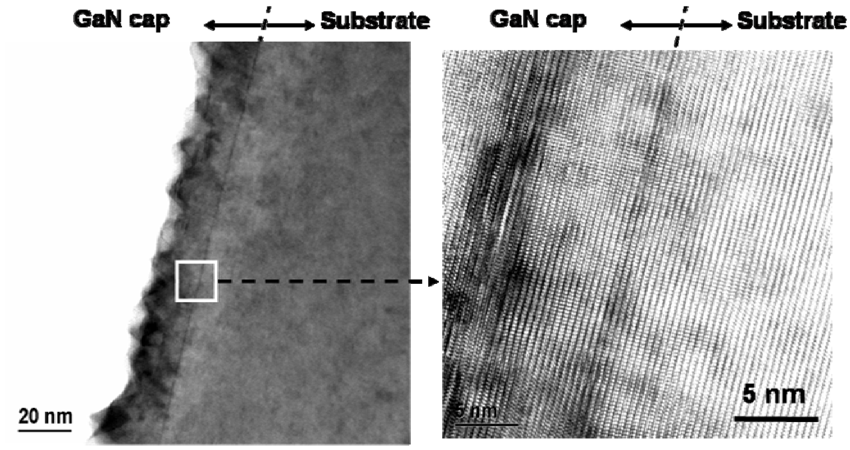


Fig. 4 Cross sectional TEM images of In-rich InGaN/GaN QD structures grown at 650 ^{o}C for 2 s.

Emission wavelength from the In-rich InGaN QDs on GaN could be controlled by changing growth parameters. We grew In-rich InGaN QDs at 650 ^{o}C and varied InGaN growth time from 2 s to 5 s. Despite the poor quality of LT-GaN capping layer, as shown in Fig. 4, strong PL emission from In-rich InGaN QDs was observed even at room temperature. By increasing InGaN growth time from 2 s to 5 s, the PL peak position was red-shifted from 404 nm to 454 nm at room temperature, as shown in Fig. 4. This phenomenon can be explained in terms of quantum confinement Stark effect (QCSE). As we can see in AFM images in Fig. 3(a) and 3(b), there was a slight increase in height of In-rich InGaN QDs by increasing InGaN growth time. It is well known that, in nitrides, there exists a huge electric field along c-axis at a level of a few MV/cm [17, 18] so that a slight increase in height of InGaN QDs would lead to significant red-shift. It is interesting to note that PL emissions from In-rich InGaN QDs were observed near UV region (~400 nm), though the reported InN band gap was below 1 eV [9-11]. The possible reasons for the near UV emission in In-rich InGaN QDs could be explained in terms of quantum confinement effect due to their small height and large band-offsets as previously reported [12].

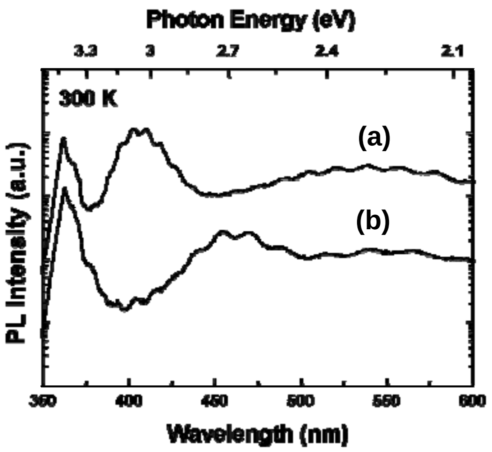


Fig. 5 Room temperature PL spectra of InGaN/GaN QD structures grown at 650 ^{o}C for (a) 2 s and (b) 5 s.

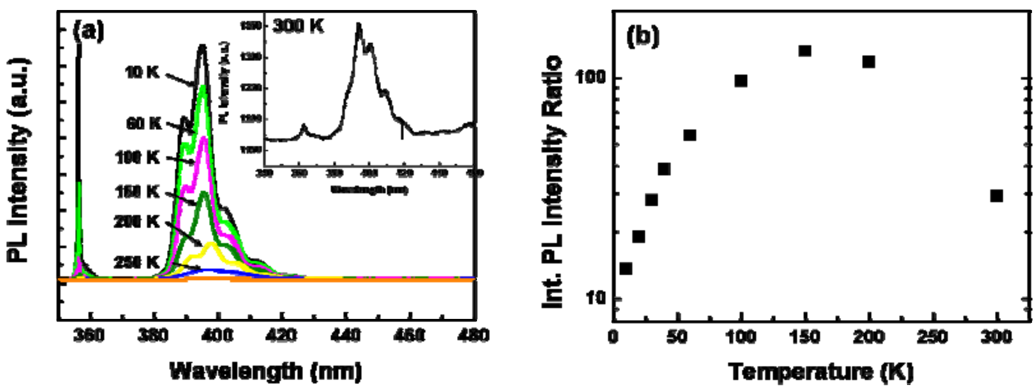


Fig. 6 (a) Temperature dependent PL spectra of InGaN/GaN QD structures grown at 650 ^{o}C for 2 s , RT PL spectra (inset), (b) integrated PL intensity ratio of InGaN QD peak to GaN band edge peak.

Temperature dependent PL experiment was performed on In-rich InGaN QDs grown on GaN for 2 s at 650 ^{o}C. The PL spectra from 10 K to 300 K are shown in Fig. 6(a). The main PL peaks from the In-rich InGaN QDs were observed at 3.14 eV, 3.18 eV at 10 K. Their peak positions were nearly unchanged by varying measurement temperature. Integrated PL intensity ratio of InGaN QDs to that of GaN band edge peak is plotted in Fig. 6(b). As the temperature increased to 200 K, the integrated PL intensity ratio increased over 100, implying that thermal stability of QDs is highly excellent. Moreover, the QD emission remained intense even at 300 K, as shown in inset of Fig. 6(a). This suggests that the strong carrier confinement in QDs leads to high radiative recombination efficiency.

3.3. Growth of In-rich InGaN/AlGaN QD structure

We introduced AlGaN barrier layers for In-rich InGaN QD growth instead of GaN to improve the 3-dimensional growth behavior and induce the blue-shift in the emission wavelength. The 100-nm-thick crack-free AlGaN barrier layer had about 30 % Al content measured by RBS and the spiral growth mode was observed by AFM, as shown in Fig. 7(a). In-rich InGaN QDs on

this $Al_{0.3}Ga_{0.7}N$ barrier layer were grown at 650 °C and InGaN growth time was varied from 2 s to 8 s. QDs grown for 2 s showed the quantum wire-like, wrinkled surface. As the growth time increased to 5 s, the wrinkled surface separated and InGaN QDs were formed, as shown in Fig. 7(c). The average diameter, height, and density of QDs were estimated as 71 nm, 4.3 nm, and 3.0 x 10^{10} /cm^2. As the growth time was further increased to 8 s, QD showed the bimodal size distribution consisted of small QDs with the density of 2.1 x 10^{10} /cm^2 and large QDs with that of 3.9 x 10^9 /cm^2. The average diameter and height of large QDs were 156 nm and 12.7 nm and those of small QDs were 62 nm and 1.8 nm, respectively. In this case, compared to InGaN/GaN QD, large QDs might be originated from the Ostwald ripening, since the height of smaller dots as well as their density decreased with the time [19]. To investigate the optical properties of In-rich InGaN/AlGaN QD structure, we capped these samples with 20 nm-thick LT-GaN layers at the same growth temperature as that of QDs.

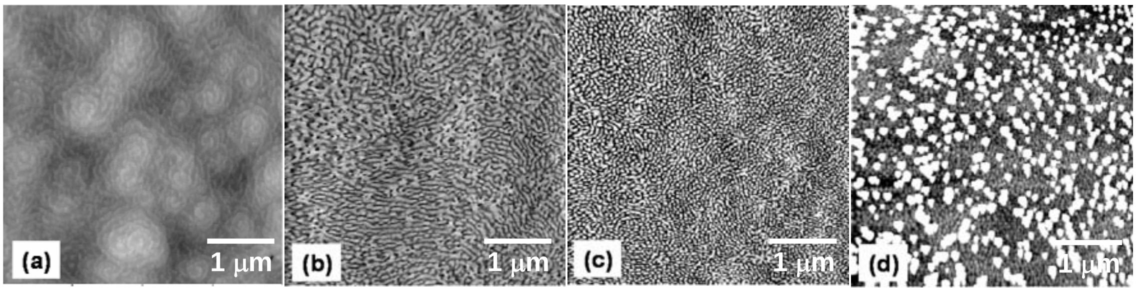


Fig. 7 4 μm x 4 μm AFM images of (a) $Al_{0.3}Ga_{0.7}N$ barrier layer and InGaN QDs grown on AlGaN at 650 °C for (b) 2 s, (c) 5 s, and (d) 8 s.

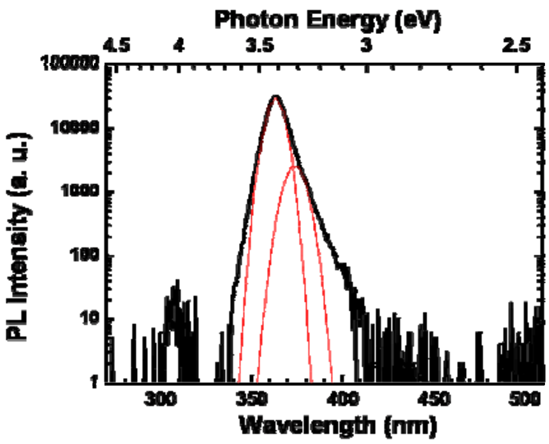


Fig. 8 Room temperature PL spectra of InGaN/AlGaN QD structures grown at 650 °C for 5 s and Gaussian fitting (red lines).

The optical properties of In-rich InGaN QDs grown on AlGaN were also examined by RT-PL using a 266 nm Nd:YAG laser. The peaks from AlGaN layer and GaN were observed at 4.01 eV and 3.44 eV respectively, whereas the luminescence from InGaN QD was not clearly distinguished from the GaN peaks, as shown in Fig. 8. However, the peak from InGaN QDs could be separated from GaN peak form Gaussian curve fitting as shown in Fig. 8. It was located at near-UV region of 3.35 eV and showed relatively weak luminescence. The origin of weak luminescence is not certain at this moment but it may be attributed to the poor quality of low-temperature GaN capping layer or the existence of many deep levels in the underlying AlGaN layer. It is expected that the optimization of low-temperature GaN capping process with less defect will enhance the luminescence efficiency.

4. CONCLUSION

Self-assembled In-rich InGaN QD structures were successfully grown by MOCVD. Low temperature growth made it possible to achieve In-rich InGaN layer with In content of 80 %. The formation of In-rich InGaN QDs was confirmed by AFM and TEM. In-rich InGaN QDs on GaN typically had an average size of 1.2 nm in height and 65.7 nm in diameter and density of 1.3 x $10^{10}/cm^2$. With the introduction of AlGaN barrier layer, the density of QDs increased to 3.0 x $10^{10}/cm^2$.

Strong PL emission from the In-rich InGaN QDs on GaN was observed at room temperature. The emission wavelength was tuned from 404 nm to 454 nm with increasing growth time. Finally, we could confirm the thermal stability of QDs from temperature dependent PL measurement. By using an AlGaN barrier layer, the PL emission was blue-shifted to 3.35 eV; however, it was relatively weak.

REFERENCES

[1] Y. Arakawa and H. Sakaki, Appl. Phys. Lett. **40**, 939 (1982).

[2] M. Asada, Y. Miyamoto, and Y. Shuematsu, IEEE J. Quantum Electron. **22**, 1915 (1986).

[3] F. Widmann, J. Simon, B. Daudin, G. Feuillet, J. L. Rouviere, N .T. Pelekanos, and G. Fishman, Phys. Rev. B **58**, R15989 (1998).

[4] Y. –T. Moon, D. –J. Kim, J. –S. Park, J. –T. Oh, J. –M. Lee, Y. –W. Ok, H. Kim, and S. –J. Park, Appl. Phys. Lett. **79**, 599 (2001).

[5] H. Hirayama, S. Tanaka, P. Ramvall, and Y. Aoyagi, Appl. Phys. Lett. **72**, 1736 (1998).

[6] B. Damilano, S. Vezian, N. Grandjean, and J. Massies, Jpn. J. Appl. Phys. **38**, L1357 (1999).

[7] C. Adelmann, J. Simon, G. Feuillet, N. T. Pelekanos, B. Daudin, and G. Fishman, Appl. Phys. Lett. **76**, 1570 (2000).

[8] Y. Arakawa, T. Someya, and K. Tachibana, phys. stat. sol. (b) **224**, 1 (2001).

[9] J. Wu, W. Walukiewicz, K. M. Yu, J. W. Ager III, E. E. Haller, H. Lu, W. J. Schaff, Y. Saito, and Y. Nanishi, Appl. Phys. Lett. **80**, 3987 (2002).

[10] V. Yu. Davydov, A. A. Klochikhin, R. P. Seisyan, V. V. Emtsev, S. V. Ivanov, F. Bechstedt, J. Furthmuller, H. Harima, A.V. Mudryi, J. Aderhold, phys. stat. sol. (b) **229**, R1 (2002).

[11] K. Xu, W. Terashima, T. Hata, N. Hashimoto, Y. Ishitai, and A. Yoshikawa, phys. stat. sol. (c) **0**, 337 (2002).

[12] H. J. Kim, H. Na, S. -Y. Kwon, H. -C. Seo, H. J. Kim, Y. Shin, G. -H. Lee, Y. -W. Kim, S. Yoon, H. J. Oh, C. Sone, Y. Park, Y. -H. Cho, Y. Sun, and E. Yoon, phys. stat. sol. (c) **7**, 2834 (2003).

[13] H. J. Kim, H. Na, S. –Y. Kwon, H. –C. Seo, H. J. Kim, Y. Shin, K. –H. Lee, D. –H. Kim, H. J. Oh, S. Yoon, C. Sone, Y. Park, and E. Yoon, J. Cryst. Growth **269**, 95 (2004).

[14] H. J. Kim, S.-Y. Kwon, S. Yim, H. Na, B. Kee, E. Yoon, J. Kim, S.-H. Park, H. Jeon, S. Kim, J. H. Seo, K. Park, M. S. Seon, C. Sone, O. H. Nam, Y. Park, Curr. Appl. Phys. **3**, 351 (2003).

[15] T. Matsuoka, H. Tanaka, T. Sasaki, A. Katsui, Inst. Phys. Conf. Ser. **106**, 141 (1990).

[16] O. Briot, B. Maleyre, and S. Ruffenach, Appl. Phys. Lett., **83**, 2919 (2003).

[17] M. Smith, J. Y. Lin, H. X. Jiang, A. Salvador, A. Borchkarev, W. Kim, and H. Morkoc, Appl. Phys. Lett, **69**, 2453 (1996).

[18] J. S. Im, H. Kollmer, J. Off, A. Sohmer, F. Scholz, and A. Hangleiter, Phys. Rev. B **57**, R9435 (1998).

[19] W. Ostwald, Z. Phys. Chem. **34**, 495 (1900).